

THE EFFECT OF HEAT TREATMENT AND CHROMIUM ADDITION ON
 γ -TITANIUM ALUMINIDE RESISTANCE TO HYDROGEN ATTACK

KHAIRMEN SUARDI

A thesis submitted in fulfillment of the
requirements for the award of the degree of
Master of Engineering (Mechanical)

Faculty of Mechanical Engineering
Universiti Teknologi Malaysia

MAY 2005

ACKNOWLEDGEMENT

Praise to Allah, the Most Gracious and Most Merciful, Who has created the mankind with knowledge, wisdom and power. Being the best creation of Allah, one still has to depend on others for many aspects directly and indirectly. This is, however, not an exception that during the course of study the author received so much of help, co-operation and encouragement that need to duly acknowledge.

First of all the author wishes to express profound gratitude to his research supervisor Assoc. Prof. Dr. Esah Hamzah for the noble guidance and valuable advice throughout the period of study. Her-ever-dynamic approach, love and dedication for promoting research and development have paved the way to attain a smooth finishing of the present study.

The author is also thankful to his Co-supervisor Assoc. Prof. Dr Ali Ourdjini, for his guidance during accomplishment of this thesis. Acknowledgements are due to Mr. Mo Zhiqiang from PSB Corporation Singapore for his assistance on TOF-SIMS analysis and Mr Liu Rong from Surface Science laboratory NUS for his assistance on MS-SIMS. The author would also like to thank the staff of Malaysian Institute Nuclear Technology (MINT) for their assistance in Galvanostatic corrosion tests. A word of gratitude is extended to the technical staffs of the Material Science Laboratory, Faculty of Mechanical Engineering University Technology Malaysia.

Special dedication to my family especially my mother for their support and encouragement. Special gratitude is reserved to all of my best friends in UTM, Rhino, Rival, Dadan, Fikri, Roni, Mr Nazori, Mr. Hadi Nur, Mr. Endra, Mr. Didik, Mr. Gigih, Maiieligan, Ong Wei Rex, Azmah Hanim, Tan Chu Li etc that I cannot mention all of them here.

ABSTRACT

The intermetallic alloys of γ -titanium aluminide are emerging as one of the most attractive alternative structural and machinery part materials for high and low temperature applications. One critical area of application is in hydrogen storage tank in chemical, oil and gas industries or in combustion engine when entail the use of hydrogen as a fuel. It has been widely reported by researchers that these materials exhibit environmental embrittlement in the presence of hydrogen, hence the diffusivity of hydrogen and the effect of hydrogen to the mechanical properties of γ -titanium aluminide is significant and technologically important. Therefore, in the present research, an investigation had been carried out to determine what causes the hydrogen attack and dealuminification. Control microstructure and phases through heat treatment by heating to 1200⁰C for 30 minutes and cooled in three different ways (i.e. water-quenched, air-cooled and furnace-cooled), and addition of a third alloying element namely chromium become the focus of this research. Samples were subjected to corrosion attack under cathodically charged with galvanostatic mode for 6, 24 and 48 hours. Hydrogen diffusion coefficient (D) was calculated based on Fick's second Law and these results were compared with that obtained from micro-Vickers hardness profiling data. The corroded and uncorroded samples were analyzed by using x-ray diffraction (XRD), scanning electron microscopy (SEM) and secondary ion mass spectroscopy (SIMS). It was found that α_2 -Ti₃Al or lamellae phases are more prone to hydrogen attack than γ -TiAl phases but γ -TiAl is more susceptible to dealuminification. Slowly cooled (furnace-cooled) Ti-Al exhibited the least hydrogen attack due to its low hydrogen diffusion coefficient. However the effect of heat treatment on dealuminification is insignificant. When γ -titanium aluminides were alloyed with chromium, their resistance towards hydrogen attack and dealuminification increased.

ABSTRAK

Aloi antara logam γ -titanium aluminida adalah salah satu bahan alternatif menarik yang membangun dengan pesat sebagai bahan struktur dan mesin pada suhu tinggi dan rendah. Aplikasi yang kritikal adalah pada tangki stor hidrogen bagi industri kimia, petrokimia dan sumber asli atau pada enjin pembakaran ketika penggunaan hidrogen sebagai sumber bahan api telah menyebabkan aloi titanium aluminida mengalami kerapuhan hidrogen. Oleh itu, keresapan hidrogen dan kesan hidrogen terhadap sifat mekanik γ -titanium aluminida adalah amat penting. Maka dalam penyelidikan ini, kajian telah dilakukan untuk menentukan kesan serangan hidrogen dan penyahaluminum. Kawalan mikrostruktur dan fasa melalui rawatan haba dengan memanaskan sehingga 1200°C selama 30 minit dan didinginkan dengan 3 kaedah yg berbeza (iaitu lindap kejut menggunakan air, pendinginan pada suhu udara dan pendinginan dalam relau), dan penambahan unsur aloian ketiga iatu kromium adalah menjadi tumpuan penyelidikan ini. Sampel dikakiskan dengan mencas katodik menggunakan mod Galvanostatik selama 6, 24 dan 48 jam. Pekali resapan hidrogen (D) dihitung melalui Hukum Kedua Fick's dan hasilnya dibandingkan dengan pekali resapan yang diperolehi daripada profil kekerasan mikro Vickers. Sampel sebelum dan selepas kakisan telah dianalisis menggunakan pembelauan sinar-x (XRD), mikroskop elektron (SEM) dan spektroskopi jisim ion sekunder (SIMS). Hasil daripada kajian ini, didapati fasa lamela atau α_2 -Ti₃Al lebih cenderung untuk mengalami serangan hidrogen jika dibandingkan dengan fasa γ -TiAl. Manakala fasa γ -TiAl lebih cenderung mengalami penyahaluminum. Sampel titanium aluminida yang dirawat haba secara pendinginan perlahan (pendinginan dalam relau) menunjukkan paling sedikit serangan hidrogen disebabkan pekali resapan hidrogen yang rendah. Walau bagaimanapun rawatan haba tidak menunjukkan kesan ketara terhadap penyahaluminum. Apabila γ -titanium aluminida dialoikan dengan kromium, ketahanannya terhadap serangan hidrogen dan penyahaluminum meningkat.

TABLE OF CONTENTS

CHAPTER	TITLE	PAGE
	DECLARATION	ii
	ACKNOWLEDGEMENTS	iii
	ABSTRACT	iv
	ABSTRAK	v
	LIST OF CONTENTS	vi
	LIST OF TABLES	xiii
	LIST OF FIGURES	xv
	NOTATIONS	xxii
	LIST OF APPENDICES	xxiv
1	INTRODUCTION	1
	1.1 Background of The Research	1
	1.2 Objective of The Research	3
	1.3 Scope of The Research	3
2	TITANIUM ALLOYS: METALLURGY AND APPLICATION	4
	2.1. Titanium Alloys	4
	2.1.1 Titanium alloy, phase transition	6
	2.2. Titanium-Aluminum Alloy	7
	2.2.1. α -Titanium aluminium alloys	9
	2.2.2. β -Titanium aluminum alloys	11
	2.2.3. α - β Titanium aluminum alloys	12

2.3.	γ -Titanium Aluminide Alloys	13
2.3.1.	Physical Properties of γ -Titanium Aluminide (γ -TiAl) Alloys	13
2.3.2.	Phase diagram and Solid State Transformation.	14
2.3.3.	Microstructure of as-cast γ -titanium aluminide	17
2.3.4.	Microstructure of heat treated γ -titanium aluminide	19
2.3.5.	Ternary Titanium Aluminide	20
2.3.6.	Mechanical Properties of γ -Titanium Aluminide Alloys.	21
2.4.	Titanium aluminide: engineering applications.	22
2.4.1.	High temperature applications.	23
2.4.2.	Low temperature applications.	27
3	CORROSION: MECHANISM AND KINETICS	30
3. 1	Introduction	30
3.2.	Hydrogen Damage	32
3.2.1.	Hydrogen blistering	32
3.2.2.	Hydrogen Embrittlement	33
3.2.3.	Hydride formation	35
3.2.4.	Hydrogen attack	35
3.3.	Dealloying and dealuminumification	36
3.4.	Environmental Resistance of γ -Titanium Aluminide Alloys.	38
3.5.	Corrosion Attack in The Form of Hydrogen Damage on γ -Titanium Aluminide.	38
3.6.	Mechanism of Hydrogen Embrittlement on γ -titanium aluminide.	40
3.7.	Sources of Hydrogen.	43
3.8.	Mechanism of Diffusion	43
3.8.1.	Nature of Diffusion Coefficient	43
3.8.2.	Mechanism of Diffusion, Activation	45

	Energy and Γ	
	3.8.3. Diffusion along Defects and on Surfaces	49
	3.8.4. Kinetics Diffusion of Hydrogen into Metal	50
3.9.	Determination of Kinetic Diffusion Coefficient of Hydrogen into γ -Titanium Aluminide using Electrochemical Galvanostatic Mode	51
3.10.	Determination of Kinetic Diffusion Coefficient of Hydrogen into γ -Titanium Aluminide using micro-hardness test	54
3. 11.	Characterization of hydride film.	56
3.11.1.	X-ray diffraction for micro-structural characterization	56
3.11.2.	Secondary Ion Mass Spectroscopy (SIMS) micro-structural characterization.	59
	3.11.2.1.Secondary Ion Mass Spectroscopy (SIMS)-Magnetic Sector SIMS	59
	3.11.2.2.Separation of secondary ions (Conventional SIMS and TOF SIMS)	65
	3.11.2.3.Static and dynamic SIMS	65
	3.11.2.4. Time of Flight (TOF) SIMS	66
3.11.3.	Scanning Electron Microscope (SEM) for Microstructure Characterization	68
3.12.	Mechanical testing of hydrides formed at the top surface using Micro-hardness Vickers testing.	69
4	RESEARCH METHODOLOGY	71
4. 1.	Introduction.	71
4. 2.	Materials	74
4. 3.	Samples Preparation	74
4. 4.	Effect of heat treatment and chromium addition on the microstructure of γ -titanium aluminide.	75
	4.4.1. Effect of heat treatment on microstructure of	75

	titanium aluminide.	
4.4.2.	Effect of chromium addition on microstructures of γ -titanium aluminide.	77
4.5.	Corrosion Testing Using Cathodically Charged Under Galvanostatic Mode	77
4.5.1.	Hydrogen Charged by Galvanostatic Corrosion Test	77
4.5.2.	Galvanostatic Corrosion Test Procedure	78
4.5.3.	Parameters Setup for Galvanostatic Corrosion Test	82
4.5.4.	Determination Diffusion Coefficient of Hydrogen into γ -Titanium Aluminide Using Galvanostatic Corrosion Test Data	82
4.6.	Phase and Microstructure Characterization.	83
4.6.1.	Optical method: image analyzer technique.	83
4.6.2.	Electron microscopy: scanning electron microscope (SEM).	84
4.6.3.	X-Ray Diffraction (XRD) method.	85
4.6.4.	Measuring Grain Size Microstructure	86
4.7.	Hydrogen ion detection: secondary ion mass spectroscopy (SIMS) on selected samples.	87
4.7.1.	Time of Flight Secondary Ion Mass Spectroscopy (TOF-SIMS)	87
4.7.2.	Magnetic Sector-Secondary Ion Mass Spectroscopy (MS-SIMS)	89
4.8.	Determination Diffusion Coefficient of Hydrogen into γ -Titanium Aluminide Using Vickers Microhardness Test	91
5	RESULTS AND DISCUSSION	93
5.1.	Introduction.	93
5.2.	Microstructure Characterization of As-cast Materials	94
5.2.1.	As-cast Ti-45%Al	94

5.2.2.	As-cast Ti-48%Al	95
5.2.3.	As-cast Ti-48%Al-2%Cr	95
5.2.4.	As-cast Ti-48%Al-4%Cr	95
5.2.5.	As-cast Ti-48%Al-8%Cr	96
5.2.6.	X-Ray Diffraction Analysis of As-received samples	97
5.3.	Microstructure Characterization and the Effect of Heat Treatment on the As-cast Ti-45%Al and Ti-48%Al	99
5.3.1.	Heat Treated Ti-45%Al Samples	99
5.3.2.	Heat Treated Ti-48%Al Samples	102
5.4.	Kinetic Diffusion of Hydrogen Attack into γ -Titanium Aluminide	105
5.4.1.	Coefficient of Diffusivity of Hydrogen into γ -Titanium Aluminide	105
5.4.2.	Coefficient of Diffusivity of Hydrogen into γ -Titanium Aluminide using Electrochemical Data Calculation	107
5.4.2.1.	Effect of Heat Treatment on the Coefficient of Diffusivity of Hydrogen into γ -Titanium Aluminide by using Electrochemical Method	108
5.4.2.2.	Effect of Chromium on the Coefficient of Diffusivity of Hydrogen into γ -Titanium Aluminide by using Electrochemical Method	111
5.4.3.	Coefficient of Diffusivity of Hydrogen into γ -Titanium Aluminide by using Microhardness Test	112
5.4.3.1.	Effect of Heat Treatment on the Coefficient of Diffusivity of Hydrogen into γ -Titanium Aluminide using Microhardness Test	113
5.4.3.2.	Effect of Chromium on the Coefficient of Diffusivity of Hydrogen into γ -Titanium Aluminide using Microhardness Test Data Calculation	115
5.4.4.	Comparison of Diffusivity Coefficient between Values Obtained from Electrochemical Method and by Microhardness Test.	116

5.4.5.	Effect of Exposure Time on the Coefficient of Diffusivity of Hydrogen into γ -Titanium Aluminide.	117
5.5.	Microstructure and Surface Morphology Analysis on effect of Heat Treatment to Corrosion Behavior	118
5.5.1.	X-ray Diffraction Analysis	118
5.5.1.1.	X-ray Diffraction Analysis on Heat Treated Ti-45%Al	118
5.5.1.2.	X-ray Diffraction Analysis on Heat Treated Ti-48%Al	124
5.5.1.3.	Comparison between α_2 -Ti ₃ Al to γ -TiAl Volume Size Expansion	128
5.5.2.	Optical and Electron Microscopy Analysis on As-received and Heat Treated γ -Titanium Aluminide After Hydrogen Attack	129
5.5.2.1.	Optical and Scanning Electron Microscope (SEM) Analysis on As-received and Heat Treated Ti-45%Al After Hydrogen Attack	129
5.5.2.2.	Optical and Scanning Electron Microscope (SEM) Analysis on As-received and Heat Treated Ti-48%Al After Hydrogen Attack	133
5.5.3.	Secondary Ion Mass Spectroscopy (SIMS) Analysis by TOF SIMS	137
5.5.3.1.	Hydrogen Mapping by TOF SIMS Analysis	139
5.6.	Microstructure and Surface Morphology Analysis on Chromium Added γ -Titanium Aluminide After Hydrogen Attack	141
5.6.1.	X-ray Diffraction Analysis on Chromium Content Variation in γ -Titanium Aluminide After Hydrogen Attack	141
5.6.2.	Optical and Scanning Electron Microscopy (SEM) Analysis	146
5.6.3.	Secondary Ion Mass Spectroscopy (SIMS) Analysis by TOF SIMS	149
5.6.3.1.	Hydrogen Mapping by TOF SIMS Analysis	150

5.7.	Magnetic Sector SIMS Analysis on Heat Treated Ti-45%Al in Comparison with Static TOF SIMS	152
------	--	-----

6 CONCLUSIONS AND RECOMMENDATION FOR FUTURE WORK

6.1	Conclusions	153
6.2	Recommendations for Future Work	154

REFERENCES	155
-------------------	------------

APPENDICES A-E	169-242
-----------------------	----------------

APPENDICES F-I	In-CD
-----------------------	--------------

LIST OF TABLES

TABLE NO.	TITLE	PAGE
2.1	Design tensile properties of unalloyed titanium sheets, strips and plates	6
2.2	Minimum and average mechanical properties of selected Titanium alloy at room temperature	8
2.3	Mechanical properties and typical applications of α titanium alloys	10
2.4	Properties of titanium aluminide alloys and superalloys	14
2.5	Comparison between the microstructures of as-cast γ -titanium aluminides	18
2.6	Effect of microstructure on mechanical properties on Ti-48Al-2Cr-2Nb	22
4.1	Chemical Composition of as-received and as-cast γ -TiAl samples	74
4.2	Heat treated samples A and B	77
4.3	Samples after corrosion test with exposure time variation	81
4.4	Galvanostatic corrosion test parameters	82
4.5	Parameters for X-Ray Diffraction (XRD) method	85
4.6	Time of Flight-Secondary Ion Mass Spectroscopy (TOF-SIMS) parameters	88
4.7	Magnetic Sector Secondary Ion Mass Spectroscopy (MS-SIMS) parameters	90
5.1	Phase compositions of as-received sample analysis by using Energy Dispersive X-ray System (EDX)	97
5.2(a)	Coefficient of diffusivity values of hydrogen into	105

	γ -titanium aluminide for as-received Ti-45%Al and Ti-48%Al samples	
5.2(b)	Coefficient of diffusivity values of hydrogen into γ -titanium aluminide for heat-treated Ti-45%Al samples	106
5.2(c)	Coefficient of diffusivity values of hydrogen into γ -titanium aluminide for heat-treated Ti-48%Al samples	106
5.2(d)	Coefficient of diffusivity values of hydrogen into γ -titanium aluminide for Ti-48%Al-2%Cr, Ti-48%Al-4%Cr and Ti-48%Al-8%Cr samples	107
5.3	Comparison of d values from x-ray diffraction analysis on uncorroded and corroded samples of heat treated Ti-45%Al before and after hydrogen attack	120
5.4	Comparison of d values from x-ray diffraction analysis on uncorroded and corroded samples of heat treated Ti-48%Al before and after hydrogen attack	126
5.5	The d values from x-ray diffraction analysis on heat treated Ti-48%Al before and after hydrogen attack	145

LIST OF FIGURES

FIGURE NO.	TITLE	PAGE
2.1	Effect of interstitial element content on the strength of titanium	5
2.2	Phase diagram of TiAl Alloys	7
2.3	Hexagonal closed packed (HCP) structure of α -titanium alloys	10
2.4	Body centered cubic (BCC) of β -titanium alloys	11
2.5	Central portion of binary Ti-Al phase diagram showing the composition ranges for two-phase engineering materials	16
2.6	Atomic arrangement (a). In ordered face-centered tetragonal (fct) $L1_0$ structure of γ (TiAl) and (b) in the ordered hexagonal DO_{19} structure of α_2 -Ti ₃ Al	16
2.7	Optical of as-cast γ -titanium aluminide, (a) equiaxed; (b) duplex; (c) nearly lamellae and (d) lamellae	18
2.8	Fully lamellae structure of heat treated Ti-48%Al	19
2.9.	(a) and (b) phase equilibria in the Ti-Al-Cr ternary system at 1200 ⁰ C and 1000 ⁰ C	21
2.10.	Engineering applications of γ -titanium aluminide, in hypersonic aircraft: (a) aerospace aircraft, X-30; (b) a military hypersonic aircraft, Aurora Mach 5; (c) civil transport aircraft, Concorde airplane. (d) applications in automotive industries	23
2.11	Cast Ti-48%Al-2%Cr-2%Nb, T-700 compressor case	24
2.12	Investment cast γ -TiAl diffuser for demonstrator	25

	aircraft engine	
2.13	Turbine wheel casting of γ -TiAl for automotive turbochargers	26
2.14	Cast γ -TiAl exhaust valves in testing for high-performance cars in US and in Europe	26
2.15	High-pressure compressor blades produced by ingot extrusion followed by closed-die forging for aircraft engine	27
2.16	Application of γ -titanium aluminide in highly hydrogen environment at hydrogen fuel storage tank in Concorde airplane	28
2.17	Application of γ -titanium aluminide expose in highly hydrogen environment: rendering of a city of fuel cell site	29
3.1	Cross section of a carbon steel plate removed from a petroleum process stream showing a large hydrogen blister. Exposure time: 2 years (taken from Imperial oil limited, Ontario, Canada)	33
3.2	Schematic diagram of hydrogen migration and blister formation	33
3.3	(a) a dezincification leaded brass bolt, 12 mm in diameter. (b) the corrosion penetrated to depth of 3 mm, causing severe porosity and embrittlement, and a remarkable layered microstructure within the corrosion product	37
3.4	Physical and Chemical Steps in Hydrogen embrittlement	40
3.5	Steady state Diffusion, Fick's First Law	45
3.6	(a) schematic of movement of an interstitial solute from A to B through #, (b) activation energy, Q_i , required through #	46
3.7	Vacancy diffusion mechanism. (a) atom movement from A to B require site B to be vacant first, (b) activation energy, Q_v , is the sum of energy to create and to move vacancy	48
3.8	Illustration of x-ray beam path	57

3.9	Schematic of interaction between x-ray and atom in material	58
3.10	(a and b) the principle of secondary ion mass spectrometry: On the sample surface, an energy rich primary ion beam generates secondary ions, which are separated and detected within a mass spectrometer. (c) flowchart showing the principle of Secondary Ion Mass Spectroscopy (SIMS)	60
3.11	Schematic representation of an ion-solid interaction, leading to the emission of neutral, excited and ionized (+ or -) target atoms (X, Y) and molecules (X Y). In surface near regions of thickness d, processes may take place which change the state of particles as emitted	61
3.12	Distribution of the original depth of sputtered atoms versus depth	62
3.13	(a) positive secondary ion spectrum of aluminium target obtained under Ar^+ bombardment, (b) negative secondary ion spectrum obtained under the same condition as figure (a)	63
3.14	Representative mass spectra for positive (the two upper spectra) and negative (the two lower spectra) secondary ions.	64
3.15	The principle of TOF SIMS	68
4.1	Flow Chart of Research Methodology	73
4.2	Schematic drawing of samples material subjected to corrosion attack	75
4.3	Schematic heat treatment temperature-time path used in heat treatment, T_α = Temperature transus α phase field, T_e = Eutectoid temperature, T_t = Temperature treatment. Q =Quenched, A=Air-cooled, FC= Furnace-cooled	76
4.4	Furnace high temperature used for heat treatment γ -titanium aluminide	76
4.5	Schematic setup of the Galvanostatic corrosion test	79
4.6	Galvanostatic corrosion test experimental setup	79
4.7	Image analyzer	84
4.8	Scanning electron microscope (SEM)	85
4.9	X-ray diffraction system (XRD)	86
4.10	Time of Flight-Secondary Ion Mass Spectroscopy	89

	(TOF-SIMS) machine in Laboratory Surface Analysis, PSB Corporation, Singapore	
4.11	Magnetic sector secondary ion mass spectroscopy (MS-SIMS) machine in Laboratory Surface Science, Faculty Physics, NUS, Singapore (b) cBN coated sample annealed at 427°C	90
4.12	Vickers microhardness machine	92
4.13	(a) Three points of indentation hardness for diffusion coefficient measurement; (b) Vickers microhardness profiling at cross-section area from the top surface into the bulk hardness.	92
5.1	Microstructures on as-received samples: (a) Ti-45% Al; (b) Ti-48% Al; (c) Ti-48% Al-2% Cr; (d) Ti-48% Al-4% Cr	96-97
5.2	X-ray Diffraction spectrums of as-received samples: (a) Ti-45% Al; (b) Ti-48% Al; (c) Ti-48% Al-2% Cr; (b) (d) Ti-48% Al-8% Cr; (e) Ti-48% Al-8% Cr	98
5.3	Classification of the α_2/γ phase equilibrium at 1000°C in the Ti-Al-Cr systems	99
5.4	Micrographs of heat treated Ti-45% Al; (a) water-quenched sample, (b) air-cooled sample and (c) furnace-cooled sample, respectively	101
5.5	Fragmented α_2 platelets in lamellae phases. Magnification 200x	101
5.6	X-ray Diffraction spectrums of heat treated Ti-45% Al samples; (a) water-quenched sample, (b) air-cooled sample and (c) furnace- (b) cooled sample, respectively	102
5.7	Optical micrographs of heat treated Ti-48% Al; (a) water-quenched sample, (b) air-cooled sample, (c) furnace-cooled sample	103
5.8	X-ray Diffraction spectrums of heat treated Ti-48% Al samples; (a) water-quenched sample, (b) air-cooled sample and (c) furnace-cooled sample	104
5.9	Bar charts showing coefficient of diffusivity of	108

	hydrogen into γ -titanium aluminide for all samples using electrochemical method	
5.10	Bar charts coefficient of diffusivity of hydrogen into γ -titanium aluminide for as-received and heat-treated Ti-45%Al samples using electrochemical method	110
5.11	Bar charts coefficient of diffusivity of hydrogen into γ -titanium aluminide for as-received and heat-treated Ti-48%Al samples using electrochemical method	111
5.12	Bar charts coefficient of diffusivity of hydrogen into γ -titanium aluminide for different chromium content samples by using electrochemical data method	112
5.13	Bar charts coefficient of diffusivity of hydrogen into γ -titanium aluminide for all samples using microhardness test	113
5.14	Bar charts coefficient of diffusivity of hydrogen into γ -titanium aluminide for as-received and heat-treated Ti-45%Al samples using microhardness test	114
5.15	Bar charts coefficient of diffusivity of hydrogen into γ -titanium aluminide for as-received and heat-treated Ti-48%Al samples by using microhardness test	115
5.16	Bar charts coefficient of diffusivity of hydrogen in γ -titanium aluminide for different chromium content samples by using microhardness test	116
5.17	(a, e and i): x-ray diffraction spectrums of Ti-45%Al on water-quenched, air-cooled and furnace-cooled samples before corrosion (hydrogen attack), respectively	119
5.18	(a, e and i): x-ray diffraction spectrums of Ti-48%Al on water-quenched, air-cooled and furnace-cooled samples before corrosion (hydrogen attack), respectively	125
5.19	Optical micrographs of heat treated Ti-45%Al after hydrogen charged; (a) to (c) are as-received samples with exposure time 6, 24 and 48 hours, respectively	130
5.20	Scanning electron micrograph of as-received Ti-45%Al after hydrogen charged for 48 hours; (a) x500; (b) x2000;	132

	(c) x100 at different location	
5.21	Scanning electron micrographs of quenched Ti-45%Al after 48 hours hydrogen charged (a) x250; (b) x300 at different location; (c) x1000 from (b)	132
5.22	Scanning electron micrographs of furnace-cooled Ti-45%Al after 48 hours hydrogen charged (a) x250; (b) x500	133
5.23	Optical micrographs of heat treated Ti-48%Al after hydrogen charged; (a) to (c) are as-received samples with exposure time 6, 24 and 48 hours, respectively	135
5.24	Scanning electron micrograph of as-received Ti-48%Al after hydrogen charged for 48 hours; (a) x500; (b) x2000	135
5.25	Scanning electron micrographs of quenched Ti-48%Al after 48 hours hydrogen charged (a) x500; (b) corroded lamellae phase, x2000; (c) corroded γ phase, x1000; (d) corroded γ phase, x2000	136
5.26	Scanning electron micrographs of furnace-cooled Ti-48%Al after 48 hours hydrogen charged (a) x250; (b) corroded lamellae phase, x500; (c) corroded γ phase, x1000 (d) surface corroded at other location, x200	136
5.27	Mass spectra result by time of flight –secondary ion mass spectroscopy (TOF SIMS); (a) As –received Ti-45%Al; (b) quenched Ti-45%Al; (c) furnace-cooled Ti-45%Al; (d): as –received Ti-45%Al; (e) quenched Ti-45%Al; (f) furnace-cooled Ti-45%Al	138
5.28	Hydrogen mapping by time of flight-secondary ion mass spectroscopy (TOF-SIMS): (a to c): as –received Ti-45%Al, quenched Ti-45%Al and furnace-cooled Ti-45%Al, respectively; (d to f): as –received Ti-48%Al, quenched Ti-48%Al and furnace-cooled Ti-48%Al, respectively	140
5.29	(a and e): x-ray diffraction spectrums of Ti-48%Al-2%Cr and Ti-48%Al-4%Cr before corrosion, respectively	143
5.30	Optical micrographs of γ -titanium aluminide with different chromium content after hydrogen charged;	147

	(a) to (c) are Ti-48%Al-2%Cr samples with exposure time 6, 24 and 48 hours, respectively; (d) to (f) are Ti-48%Al-4%Cr samples with exposure time 6, 24 and 48 hours, respectively; (g) to (i) are Ti-48%Al-8%Cr with exposure time 6, 24 and 48 hours, respectively	
5.31	Scanning electron micrographs of Ti-48%Al-2%Cr after hydrogen charged for 48 hours; (a) corroded γ phase, x2000; (b) corroded lamellar phase, x2000	148
5.32	Scanning electron micrographs of Ti-48%Al-4%Cr after hydrogen charged for 48 hours; (a) x250; (b) corroded lamellar phase, x2000; (c) corroded γ phase, x2000	148
5.33	Scanning electron micrographs of Ti-48%Al-8%Cr after hydrogen charged for 48 hours; (a) x125; (b) corroded β phase, x500; (c) corroded lamellae phase, x2000; (d) corroded γ phase, x125	149
5.34	Mass spectra result by time of flight –secondary ion mass spectroscopy (TOF SIMS); (a): as –received Ti-48%Al, (b) as-received Ti-48%A-2%Cr, (c) as-received Ti-48%Al-4%Cr and (d) as –received Ti-48%Al-8%Cr	150
5.35	Hydrogen mapping by time of flight-secondary ion mass spectroscopy (TOF-SIMS): (a): as –received Ti-48%Al, (b) as-received Ti-48%A-2%Cr, (c)as-received Ti-48%Al-4%Cr and (d) as –received Ti-48%Al-8%Cr	151
5.36	Secondary ion mass spectroscopy (SIMS) on water-quenched Ti-45%Al after hydrogen attack	152

NOTATIONS

γ	-	Gamma Phase/ tetragonal atomic structure
α	-	Alpha phase/ hexagonal atomic structure
α_2	-	Alpha two phase/ hexagonal closed packed atomic structure
β	-	Betha phase/ cubic atomic structure
at. %	-	Atomic percentage
Γ	-	Average jump frequencies
C	-	Concentration of diffusing species (hydrogen)
Z	-	Charge number of electro-active diffusing species
F	-	Faraday constant
S	-	Sectional area common to both electrode and electrolyte
D	-	Kinetic diffusion coefficient
I	-	Constant current
L	-	Sample half thickness
V_m	-	Volume molar
E	-	Potential
$dE/d\delta$	-	Potential variation of the electrode (γ -TiAl) with the change in hydrogen composition
Hv	-	Microhardness vickers
erf	-	Error function
λ	-	wave length
d	-	interplanar spacing
hkl	-	milller indices
θ	-	diffraction angle
a, b, c	-	lattice constant
\AA	-	Amstrong constant

SEM	-	Scanning Electron Microscope
XRD	-	X-ray Diffraction
NA	-	Number of grain
f	-	Jeffries's constant
SIMS	-	Secondary ion mass spectroscopy
TOF-SIMS	-	Time of flight-secondary ion mass spectroscopy
KeV	-	Kilo electron volt

LIST OF APPENDICES

APPENDIX	TITLE	PAGE
A	List of Publications	169
B	Parameters Setup for Galvanostatic Corrosion Test	186
C	Diffusion Coefficient Calculation from Galvanostatic Corrosion Test Data	192
D	Diffusion Coefficient Calculation from Microhardness Test Data	216
E	Details of X Ray Diffraction Spectrums	242
F	Details of Secondary Ion Mass Spectroscopy Spectrums By TOF-SIMS	In-CD
G	Details of Hydrogen Mapping Analysis by TOF-SIMS	In-CD
H	Details of Magnetic Sector SIMS Spectrums	In-CD
I	Details of Potential Data from Galvanostatic Electrochemical Test	In-CD

CHAPTER I

INTRODUCTION

1.1. Background of The Research

Since titanium was first discovered in 1790 and was mass-produced in the early 1950's [Mangonon, 1999], the development and research on titanium and its alloys have been well developed. Until now, scientists and engineers had discovered new advanced material: gamma titanium-aluminide, well known as " γ -TiAl". γ -TiAl based alloys with compositions ranging from 45 to 50 at.%Al, is an intermetallic compound consist of Ti_3Al (α_2 -phase) and Ti-Al (γ -phase) with low density, high Young's Moduli, good creep and oxidation resistance up to 900°C (creep limit) [ASM, 1994]. Due to their high properties, this γ -TiAl extent the capabilities of titanium-based alloys beyond that of conventional α - β titanium alloys and potentially viable to replace nickel-based super alloys in some application with a material having one-half the density [Zheng *et al.*, 1995; Cheng *et al.*, 1999; Nombela *et al.*, 2000]. This γ -TiAl have been considered attractive candidates for applications in advanced fields such as in aerospace: blades, body frames, compressor cases, discs; in marine applications: turbocharger rotors, flywheel, turbine engine compressor component, and turbine engine exhaust system components; in automotive engine components and in chemicals and other applications: hydrogen storage tank,

chemical storage tank and medical profession. [Mangonon, 1999; ASM, 1994; Seagle and Wood, 1993; Huang and Chessnut, 1994; Kim and Dimiduk, 1991 and Maeland *et al.*, 1999] .

The future of titanium aluminide intermetallics is bright and well developed deformation mechanisms theory can explain the relationship between mechanical properties and microstructure. The fundamental understanding of phase stabilities is enabling the optimization of microstructure and properties.

In normal air condition, γ -Titanium aluminide intermetallics are known to be highly resistant to atmospheric corrosion at room temperature. However, their tendency to oxidize to form Al_2O_3 preferentially to TiO_2 exists only up to 850°C , which is known as high temperature corrosion [Kim and Dimiduk, 1991]. However, at room temperature γ -titanium aluminide is often subjected to hydrogen-damage mechanisms, although the surface oxide film forms barrier to hydrogen atom entry to metal lattice. It is already known that titanium alloys are susceptible to hydrogen to form hydride on the surface. Hydrogen causes embrittlement leading to the deterioration of the properties of the alloys [Sha and Mckinven, 2002]. Much effort has been made to quantify the hydrogen susceptibility and its effect to properties of titanium alloys. Takasi *et al.* [1994] noted that for Gamma TiAl alloy, the yield strength increased with increasing amount of hydride but the ultimate tensile strength, ductility and fracture toughness decreased [Takasi *et al.*, 1994]. Therefore the amount of hydrogen that a titanium alloy can absorb during service is a major measure of the ability of the alloy to retain good properties [Sha and Mckinven, 2002]. Also, some researchers found that hydride formed on the surface and the possibility that some hydrogen may occupy the interstitial sites in the alloy [Takasaki *et al.*, 1994; Gao *et al.*, 1993 and Sundaram *et al.*, 2000].

It was found that hydrogen attack is more likely to occur in α_2 or lamellae phases rather than γ -TiAl phases. Control of microstructure and phases could be the

answer to this problem. Appropriate γ -titanium aluminide which is more resistant to environment embrittlement and has useful properties need to be investigated. The focus of this research is to investigate the influence of microstructure and an alloying element content in γ -titanium aluminide namely chromium to corrosion attack in the form of hydrogen attack or hydrogen embrittlement.

1. 2. Objectives of the Research.

The objective of this research is to study the effect of microstructure variation by heat treatment process and chromium addition on γ -titanium aluminide resistance to hydrogen attack and dealuminification.

1. 3. Scope of the Research.

The scope of the research include:

1. Investigation of the effect of microstructure of γ - titanium aluminide generated by heat treatment on corrosion attack in the form of hydrogen attack.
2. Investigation of the influence of an alloying element, namely chromium, added to γ -titanium aluminide on corrosion in the form of hydrogen attack.
3. Investigating the effect of microstructure and chromium content on corrosion kinetics; namely coefficient of diffusivity of hydrogen in γ -titanium aluminide
4. Investigating the hydride formed on the surface of titanium aluminides.

6.2 Recommendations for Future Work

Further research can be carried out to enhance the current research and the following are areas which are recommended for further investigation;

1. In-depth investigation on the mechanical properties namely; tensile, fatigue and creep strength of γ -titanium aluminide after it is subjected to hydrogen attack and dealuminification.
2. Metallurgical and microstructural study in other ternary titanium aluminides such as, Ti-48%Al-X%(Nb, V, Mo, Mn), and in-depth investigation on the effect of heat treatment to corrosion behavior of the ternary titanium aluminide. Understanding microstructural control through combination of heat treatment and addition of third alloying element which may produce better microstructures that more resistant to hydrogen attack and dealuminification.
3. Study on the heat treated alloyed γ -titanium aluminide and its effect on corrosion

REFERENCES

- Abanto-Bueno, J. L., Sundaran, P. A. and Clemens, H. (1997). Effect of Hydrogen on The Tensile Properties of a Ti-47Al-2Cr-0.2Si Sheet Under Electrolytic Charging Conditions. *Scripta Materialia*. **Vol. 38**: 149-155.
- Abdul-Hamid, O. S. and Latanison, R. M. (1996). *Hydrogen Effects in Materials*, TMS, Warrendale, PA, p. 205.
- Abe, E., Gao, K. W., and Nakamura, M. (2000). Local Amphophization in Hydrogen Charged Two-Phase TiAl Alloy. *Scripta Materialia*. **Vol. 24** : 1113-1118.
- Appel F, et al., (2000). *Recent progress in the development of gamma titanium aluminide alloys, advanced engineering materials*. USA: Wiley Interscience. **Vol. 8**: 699–720.
- Appel, F. and Wagner, R. (1998). Microstrcutural and Deformation of Two-Phase γ -Titanium Aluminides. *Materials Science and Engineering R*. **Vol. R22**: 187-268.
- Armbruster, M. H. (1943). The Solubility of Hydrogen at Low Pressure in Iron, Nickel and Certain Steel at 400 to 600⁰C. *J. Am. Chem. Soc.* **Vol. 65**: 1043– 1054.
- ASM International (1987). *Material Properties Handbook Titanium Alloys*.USA.

- ASM International (1994). *Materials Properties Handbook: Titanium Alloys*. USA. Design. International Edition. New Jersey, USA: Prentice-Hall, Inc.
- ASM International (1996). *Binary Alloy Phase Diagrams Vol.1*. USA.
- Austin, C.M., and Kelly, T.J (1993). In. *Proc. International Symposium on Structural Intermetallics*(eds R. Darolia, J.J. Lewandowski, C.T.Liu, P.L.Martin, D.B.Miracle, and M.V. Nachal), TMS, Warrendale, PA,p.143.
- Baur, H and Smarsly W (2000). Potential of TiAl for industrial applications. *Euromat Proceeding*. October. Munich, Germany: abstract.
- Beachem, C. D. (1972). A New Model for Hydrogen-Assisted Cracking (Hydrogen “Embrittlement”). *Metall. Trans.* **Vol. 3**: 437-451.
- Benninghoven, A. (1973). Surface investigation of solids by the statical method of secondary ion mass spectroscopy (SIMS). *Surface Sci.* **Vol.35**: 427–457.
- Benninghoven, A. (1975). Developments in secondary ion mass spectroscopy and applications to surface studies. *Surface Sci.* **Vol.53**: 596–625.
- Benninghoven, A. (1985). Static SIMS applications – From silicon single crystal oxidation to DNA sequencing. *J. Vac. Sci. Technol. A* **Vol.3**: 451–460.
- Benninghoven, A. (1994). Surface analysis by secondary ion mass spectroscopy (SIMS). *Surface Sci.* **Vol.299/300**: 246–260.
- Birnbaum, H. K. (1987). Environmental Sensitive Fracture of Metals and Alloys. *Proc. Office Naval Research Workshop*. June 3-4. Washington DC: p.105.

- Blackburn, M. J. (1970). *The Science Technology and Applications of Titanium*. London: Pergamon Press, London. pp.663.
- Blum M, et al., (2001). *Commissioning of a prototype plant for economical mass production of TiAl valves*. Wyoming USA: TMS. p. 131–8.
- Bockris, J. O. M., McBreen, J., Nanis, L. (1965). *J. Electrochem. Soc.* **Vol. 112**: 025–1031.
- Brady. M. P., Smialek. JL., Smith. J. and Humphrey. DL. (1997). The Role of Cr in Promoting Protective Alumina Scale Formation by γ -Based Ti-Al-Cr Alloys-I Compatibility with Alumina and Oxidation Behavior in Oxygen. *J. Acta Mater.* **Vol 45**; 2357-2371.
- Brass, A. M and Chene, J. (1999).Hydrogen Absortion in Titanium Aluminides Exposed to Aqueous Solution at Room Temperature. *J. Material, Science and Engineering*, **Vol.A.(272)**: 269-278.
- Brass, M and Chene, J. (1998). Hydrogen Absorption in $\alpha_2+\gamma$ Titanium Aluminides During Mechanical Grinding. *Scripta Materialia*. **Vol. 39**: 1569-1575.
- Callister, J. R and William, D. (2000). *Material Science and Engineering an Introduction*. 5th .ed. New York: John Wiley and Sons. 38-65.
- Chandley D. (2000). Use of gamma titanium aluminide for automotive engine valves. *Metallurgical Science and Technology*. **Vol. 18**: 8–11.

- Chen, M. and Lin, T. L. (1990), The Influence of Lamellar Structure on the Crack Propagation in Two Phase TiAl alloys. *J. Gamma Titanium Aluminides, The Mineral, Metals and Materials Soc*, pp.533-542.
- Cheng, T.T., M.R Willis and L.P Jones. (1999). Effect of Major alloying additions on Microstructure and Mechanical Properties of γ -TiAl. *Intermetallics*. **Vol. 7**: Issue 1: 89-99.
- Chu, Wu Yang and Thompson, A.W. (1991). Effect of Hydrogen as a Temporary β Stabilizer on Microstructure and Brittle Fracture Behavior in a Titanium Aluminide Alloy. *Metallurgical Transactions A*. **Vol. 22**: 71-81.
- Combres, Y., Tsuyama, S. and Kishi, T. (1992). Surface precipitation after cathodic charging of hydrogen and heat treatment in air for the TiAl intermetallic compounds *Scripta Metallurgica et Materialia*. **Vol. 27**: 509-514.
- Crank, J. (1967). *The Mathematics of Diffusion*. 2nd Edition. London: Oxford University Press. pp 11-27.
- Cullity, B. D. (1956). *Element of X-ray Diffraction*. Reading. Massachusetts: Addison Wesley. pp 459-461.
- Deny, A. Jones. (1992). *Principles and Prevention of Corrosion*. 2nd ed, Maxwell Macmillan International Edition, Singapore. pp.334-335.
- Devanathan, M. A. V. and Stachurski, Z. (1966). *J. Electrochem. Soc.* **Vol. 113**: (1966) 619-623.

- Dogan. B., Schoneich. D., Schwalbe., Wagner. R. (1996). Fatigue precracking and fracture toughness testing of TiAl intermetallics. *J.Intermetallics*. **Vol. 4:** 6169.
- Ence, E., Farrar, P.A and Margonin, H. (1960). Binary and ternary diagrams of the Ti-Al-Cr and Ti-Al-V systems. *Wright Air Development Division Tech. Report*; 1-20.
- Fiermans, L., Vennik, J. and Dekeyser, W. (1978). *Electron Microscopy and Ion Spectroscopy of Solids*. Plenum Press. New York. 324 – 435.
- Fontana, M. G. (1986). *Corrosion Engineering*. 3rd ed, Mc Graw-Hill, New York. pp 144-145.
- Gao, J. Wang, Y. B., Chu, W. Y. and Hsiao, C. M. (1992). Study on Hydride in TiAl After Cathodic Charging. *Scripta Metallurgica et Materallia*. **Vol: 27:** 1219-1222.
- Gao, J., Wang, T. B., Chu, W. Y., C.M.Hsiao (1993). *J. Science Metals & Matter*. **Vol. 27:**1483.
- Gao, K. W and Nakamura, M. (2000). Effect of Hydrogen on Tensile Properties of Ti-49%Al Alloy. *Scripta Materialia*. **Vol. 43:** 135-140.
- Gray, H. R. (1974), Testing for Hydrogen Environmental Embrittlement: Experimental Variables. *Hydrogen Embrittlement Testing, ASTM STP 543, American society for Testing and Materials*, pp 133-151.
- Habel, U., Polock, T. M and Thompson. A. W. (1996). *Hydrogen Effects in Metals*. Warendale, PA: TMS. P.787.

- Hamzah, E., Suardi, K., Ourdjini, A. and Lau, K. W. (2003). Effect of heat treatment on microstructure and hardness of γ -base titanium aluminide. *Journal of The Institute Materials Malaysia*. **Vol. 4:** 83 – 101.
- Hashi, K., Ishikawa, K., Suzuki, K. and Aoki, K. (2000). Hydrogen Induced Amorphization in off-Stoichiometric Ti_3Al . *J. Scripta Materialia*. **Vol.44:** 2591-2595.
- Haruna, T., Iwata, T., Sundararajan, T. and Shibata, T. (2002). Environment Assisted Cracking of Gamma Titanium Aluminide in Aqueous Sulfate Solutions. *Material Science Engineering A*. **Vol. 329-331:** 745-749.
- Haubold, T. (2000). Testing of forged g-TiAl high pressure compressor blades. *Aeromat Proceeding*. June. Seattle USA: abstract.
- Heiderbach, R. H and Verink, E. D. (1972). The Dezincification of Alpha and Beta Brasses. *Corrosion*. **Vol. 28 (11):** p.397.
- Hirth, J. P. (1987). Environmental Sensitive Fracture of Metals and Alloys. *Proc. Office Naval Research Workshop*. June 3-4. Washington DC: p.79.
- Huang, S.C., Chessnut, J. C. (1994). Gamma TiAl and its alloys. *J.Intermetallic Compound*, **Vol.2**.
- Iyer, R. N. and H.W. Pickering and Zamanzadeh, M. (1989). Analysis of Hydrogen Evolution and Entry in Metals for the Coupled Discharged-Recombination Mechanism. *J. Electrochem. Soc.* **Vol. 136:** 2463–2470.

- Iyer, R. N. and H.W. Pickering. (1990). Mechanism and Kinetics of Electrochemical hydrogen Entry and Degradation of Metallic System. *Annu. Rev. Mater. Soc.* **Vol. 20**: 299–338.
- Jewett, T. J., Ahrens B, Dahms M. (1997). Stability of TiAl in the Ti-Al-Cr system. *J. Mater Sci Eng.* **Vol: A225**: 29-37.
- Kainuma, R., Ohnuma, I., Ishikawa, K., Ishihida, K. (2000). Stability of B2 ordered phase in the Ti-rich portion of Ti-Al-Cr and Ti-Al-Fe ternary systems. *J. Intermetallics.* **Vol 8**; 869-875.
- Kenneth, R. T. and John, C. (1995). *Corrosion for Science and Engineering*. 2nd edition. Singapore: Longman Singapore (Pte) Ltd.
- Kim, Y.W., Dimiduk, D. M. (1991). Progress in The Understanding of Gamma Titanium Aluminides; *Journal of the Minerals, Metal and Materials Society*, **Vol 43 (8)**: 40 47.
- Kim, Y.W. (1991). Microstructural Evolution and Mechanical Properties of a Forged Gamma Titanium Aluminide Alloy, *JOM*, 1121-1122
- Kim, S.E., Lee, Y. T., Oh, M. T., Yamaguchi, M. (1995). Effect of α_2 on mechanical properties of a TiAl alloy. In: Kim, Y. W., Wagner, R., Yamaguchi, M. ed. Gamma titanium aluminides. The *Minerals, Metals and Materials Soc.*, 1995. p. 737-744.
- Kovacs, T. (1969). *Principles of X-ray Metallurgy*. Plenum Press. New York. 68 – 79.

- Kumar, A. and Balasubramaniam, R. (1997). Effect of Cathodically Charged Hydrogen in Titanium Aluminides Studied by Microhardness Profiling. *Materials Science and Engineering A*. **Vol. A237**: 132-136.
- Latanision, R. M. and Kurkela, M. (1983). Hydrogen Permeability and Diffusivity in Nickel and Ni-Base Alloy. *Corrosion*. **Vol. 39**: 174– 180.
- Latanision, R. M. and Staehle, R. W. (1969). Plastic Deformation Electrochemically Polarized Nickel Single Crystals. *Acta Met.* **Vol.17**: 307.
- Li Leach, J. S., Saunders, S. R. (1966). *J. Electrochem. Soc.* **Vol. 113**: 681–687.
- Liu, C. T. and McKerney, C. G. (1990). Environmental Embrittlement- a Major Cause of Low Ductility of Ordered Intermetallics. *J.High Temperature Aluminide and Intermetallics, The Minerals, Metals and Materials Soc.* pp 135-151.
- Loria E. A. (2000). Gamma titanium aluminides as prospective structural materials. *Intermetallics*. **Vol. 8**:1339–1345.
- Maeland, Hauback, B., Fjellvag, H., Sorby, M. (1999). The Structure of Hydride phases in the Ti₃Al/H System. *J. International Journal of Hydrogen*. **Vol. 24**: 163-168.
- Malcolm. A. Fullenwider, *Hydrogen entry and action in metals*. Pergamon Press, USA, pp. 80.
- Mangonon, Pat L. (1999). *The Principles of Materials Selection for Engineering*. International Edition, Prentice-Hall, Inc. USA.

- Manor, E. and Eliezer, D. (1989). Hydrogen Effect in Ti₃Al-Nb Alloy. *Scripta Metallurgical Materials*. **Vol. 23**: 1313-1318.
- Matsui, H., Kimura, H. and Moriya, S. (1979). The effect of hydrogen on the mechanical properties of high purity iron I. Softening and hardening of high purity iron by hydrogen charging during tensile deformation *Mater. Sci. Eng.* **Vol. 40**: 207.
- McQuay, P. A. (2001). *Cast gamma TiAl alloys: are we there yet?*. Wyoming USA: TMS. p. 83-90.
- Mitao, S., Tsuyama, S and Minakawa, K. (1991). Effect of Microstructure on the Mechanical Properties and Fracture of Gamma-base Titanium Aluminide. *Material Science and Engineering A*. **Vol. A143**: 51-62.
- Naka, S., Thomas, M., Scanchez, C. and Khan, T. (1997). *Structural Intermetallics*. TMS, Warrendale, PA; p. 313.
- Nakamura H., Takeyama W. L., Yamabe Y., Kikuchi M. (1993). *Proc.3rd Jpn Int. SAMPE Symp*; 1353.
- Nickel, H., Zheng, H., Elschner, A. and Quadakkers, W. J. (1995). *Microchim, J. Acta Materialia*. **Vol. 23**: 119.
- Nombela, M., V.Kolarik, M. Grob, H.Fietzek and N. Eisenreich. (2000). In situ study of the scale formation on γ -TiAl. *Materials At High Temperature*. **Vol. 17**: Issue 1.
- Oriani, R. A. (1978). Hydrogen Embrittlement of Steels. *Ann. Rev. Mater. Sci.* **Vol. 8**: 327.

- Perng, T. P. and Wu, J. K. (2003). A brief review note on mechanisms of hydrogen entry into metals. *Materials Letters*. **Vol. 57**: 3437– 3438.
- Petch, N. J. and Stables, P. (1952). A Decohesion Theory for Hydrogen-Induced Cracks Propagation. *Nature*. **Vol. 169**: 852.
- Recina, V (2000). Mechanical Properties of Gamma Titanium Aluminides. Chalmers Technical University: Ph. D. Thesis.
- Roy, T. K., Balasubramaniam, R. and Ghosh, A. (1996). Determination of Oxygen and Nitrogen Diffusivities in Titanium Aluminide by Subscale Microhardness Profiling. *J. Scripta Mater*. **Vol. 34**: 1425.
- Roy, T. K., Balasubramaniam, R. and Ghosh, A. (1996). Determination of Oxygen and Nitrogen Diffusivities in Titanium Aluminide by Subscale Microhardness Profiling. *J. Scripta Mater*. **Vol. 34**: 1425.
- Ruales, M., Martell, D., Vazquez, F., Just, F. A and Sundaram, P. A. (2002). Effect of Hydrogen on the Dynamic Elastic Modulus of Gamma Titanium Aluminide. *Journal of Alloys and Coumpounds*. **Vol. 339**: 156 – 161.
- Rugg, D. (1999). *Titanium aluminides—great potential but not yet*. Wyoming USA: TMS. p. 11–14.
- Sauthoff, G. (2000). Multiphase intermetallic alloys for structural applications, *Intermetallics*. **Vol. 8**: 1101-1109.

- Schafrik RE, (2001). *A perspective on intermetallic commercialization for aero-turbine applications Structural intermetallics*. Wyoming USA: TMS.
- Seagle, S. R., Wood, J. R. (1993). Advances in Titanium Alloys, *J.Key Materials Engineering*, vol77-78, pp 91-102, Transtech Publication, Switzerland.
- Sha, W., McKinven, C. J. Experimental Study of The Effect of Hydrogen Penetration on Gamma titanium aluminide and Betta 21S Titanium alloys. *J. Alloys and Compounds*, 2002, Vol. L16-L20, pp. 335.
- Shao, G., Tsakiropoulos, P. (1999), Solidification structures of Ti-Al-Cr alloys. *J. Intermetallics*. **Vol 7**: 579- 587.
- Shewmon, P. J. (1965). *Diffusion in Physical Metallurgy*, R. W. Cahn, ed., North-Holland Publishing Company, Amsterdam. p. 365.
- Shin, D.S., Scarr, G.K. and Wasielewski, G.E. (1989). On hydrogen Behavior in Ti_3Al . *Scripta MetallurgicalMaterial*. **Vol. 23**: 973-978.
- Stephan, T. (1999). *TOF-SIMS in Cosmochemistry*. Munster, Germany: Faculty of Mathematics and Natural Resources University of Munster: pp. 1-46.
- Strafford, K. N and Towell, J. M. (1976). *J. Oxidation of Metal*. **Vol.10**: 41.
- Sundaram, P. A., Basu, D., Steinbrech, R. W., Ennis, P. J., Quadakkers, W. J. and Singheiser, L. (1999a). Effect of Hydrogen on the Elastic Modulus and Hardness of Gamma Titanium Aluminides. *Scripta Materialia*. **Vol. 41**: 839–845.

- Sundaram, P. A., Wessel, E., Clemens, H., H. Kestler, P.J. Ennis, W.J. Quadakkers and Singheiser, L. (2000). Determination of Diffusion Coefficient of Hydrogen in Gamma Titanium Aluminides During Electrolytic Charging. *Acta Materialia*. **Vol. 48:** 1005-1009.
- Sundaram, P. A., Wessel, E., Ennis, P. J., Quadakkers, W. J and Singheiser, L. (1999b). Diffusion Coefficient of Hydrogen in A Cast Gamma Titanium Aluminide. *Scripta Materialia*. **Vol. 41:** 75-80.
- Tabata, T. and Birnbaum, H. K. (1983). Direct Observations of The Effect of Hydrogen on The Behavior of Dislocations in Iron. *Sci. Metall.* **Vol. 17:** 947.
- Takasaki, A. and Furuya, Y. (1996). Hydrogen Evolution from Chemically Etched Titanium Aluminides. *J. Alloys and Compounds*. **Vol. 243:** 167-172.
- Takasaki, A. and Furuya, Y. (1998). Hydride Formation and Thermal Desorption Spectra of Hydrogen of Cathodically Charged Single-Phase Gamma Titanium Aluminide. *Scripta Materialia*. **Vol. 40:** 595-599.
- Takasi, A., Ojima, K. and Taneda, Y. (1994). Hydride Formation in Two-Phase (Ti₃Al + TiAl) Titanium Aluminides During Cathodic Charging and Its Dislocations. *Journal Alloy Compounds*. **Vol. 216:** 1-6.
- Tetsui, T. (2000). Development of TiAl turbocharger for passenger vehicles. *MRS symposium*. November. Boston USA: High-Temperature Ordered Intermetallic Alloys IX.
- Thompson, A. W. (1988). *Environmental Effect on Advances Materials*. ed.R.E.p.21, TMS-AIME, Warrendale, PA.

Thompson, A. W. (1992). Effect of Hydrogen in Titanium Aluminide alloys.

Material Science and Engineering A. **Vol. A153**: 578 - 583.

Triano, A. R. (1985). *Hydrogen Embrittlement and Stress Corrosion Cracking*. 2nd edition. Metal Park, Ohio: ASM.

Troiano, A. R. (1960). *Trans. ASM*. **Vol. 52**: 54.

Verink, E. D. and Heiderbach, R. H. (1972). *ASTM STP 516*. Philadelphia: ASTM.

Voice W *et al.*, (1999). *The future use of gamma titanium aluminides by Rolls Royce*. Wyoming USA: TMS. p. 397–400.

Web 1: <http://www.aerospaceweb.org/design/waverider/examples.shtml>

Web 2: <http://www.concorde-jet.com/index.php>

Web 3: <http://www.corrosionsource.com/cost/CorrosionCostUS.htm>

Wen, C. J., Ho, C., Boukamp, B. A., Raistrick, I. D., Weppner, W. and Huggins, R. A. (1981). Use of electrochemical methods to determine chemical-diffusion coefficients in alloys; Application to lithium- aluminum. *Int. Metall. Rev.* **Vol. 26**: 253.

Wilhemsen, W. (1990). Electrochemical and SIMS Studies of Cathodically Formed Hydride Layers on Titanium. *J. of Electrochemical*. **Vol. 32**: 1913-1917.

- Wu, J. K. (1992). Electrochemical Method for Studying Hydrogen in Iron, Nickel and Paladium. *Int. J. Hydrogen Energy*. **Vol. 17**: 917– 921.
- Yang, K. and Edmonds, D. V. (1993). Effect of Hydrogen as a Temporary Alloying Element on the Microstructure of Ti₃Al Intermetallic. *Scripta Metallurgical et Meterial*. **Vol. 28**: 71-76.
- Zapffe, C and Sims, C. (1941). *Trans. AIME*. **Vol. 145**: 225.
- Zeller, A., Dettenwanger, F. and M.Schutze (2002), "Influence of Water Vapor on The Creep and Fatigue Properties of TiAl", *J.Intermetallics*, **vol.10**,pp.33-57.
- Zheng, N., W.J Quadakkers, Gil, A., and Nickel, H.. (1995). Studies concerning the effects of Nitrogen on the Oxidation behaviour of TiAl-based intermetallics at 900°C. *Oxidation of Metals*. **Vol.44**:477-499.